

Understanding Nuclear Magnetic Resonance

An Honors Thesis (HONR 499)

by

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Abstract

Scientists often try to find ways to better explain what governs the universe. Many of these theories and methods are applied by using technology. One such method is Nuclear Magnetic Resonance (NMR). NMR uses an internal property of an atom, called spin, to reveal information about the subject in question. For example, chemists can use NMR to reveal how many hydrogen or carbon atoms are in a molecule. This is done through altering the spin states. The most well-known application of this science is in the use of Magnetic Resonance Imaging (MRI) machines in the medical field. My interest is in the physics behind the NMR technique and how to use the information that the technology captures. My studies tested light mineral oil by using a spectrometer to alter the spin states. Measurements were taken to determine the relaxation times for the spins in mineral oil.

Acknowledgements

I would like to thank Dr. David Grosnick for being my advisor for this project. He has been a helpful guide, not only during my thesis process, but throughout my entire collegiate career at Ball State University.

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Process Analysis Statement

When I began my thesis process, I was not sure what I wanted to do. I asked Dr. Grosnick if there were any research opportunities in the Physics Department that I could get involved with. He ended up suggesting three potential experiments that were not being worked on. I cannot remember the other options at this point, but I chose Nuclear Magnetic Resonance (NMR) because it sounded the most interesting, and it is the science behind Magnetic Resonance Imaging (MRI) machines, something I was already vaguely aware of. I wanted to learn how an MRI image captures what it does and how the technology itself works. I have always been drawn to physics because it explains what governs the universe. I enjoy finding out why things work, exist, or behave in the manner that they do.

Doing experiments with the NMR apparatus was a completely new experience for me. While I have done experiments before, the topics were always discussed thoroughly in class beforehand. My professors could answer any questions I had or clarify topics I struggled to understand. The same cannot be said for my thesis as I have not taken a course that explicitly discusses NMR. There were no experts of the equipment available, so any issues faced had to be resolved primarily on my own. This experience taught me to use my own resources to understand the topic. Much outside research was required prior to beginning any work with the equipment. I also needed to apply various quantities and processes that I have learned throughout my collegiate career.

The hardest challenge for me to overcome was working alone. Until my thesis, I had always had one or more partners for experiments during my collegiate career. Having a partner means that you have access to someone with a different thinking process than yourself. They will

approach situations with ideas that you may not even think of yourself. During the times I did not have a partner, the entire class was working on the same assignment. If I was stuck on a step, I could ask one of my peers for advice or potential methods that could help. Without either of these options available, certain steps of my experiment were met with slow progress. One of my largest and most recurring problems concerned the oscilloscope. I had only used it one class before, and I was not comfortable with operating it alone. I had to constantly refer to its manual and conduct various Google searches to ensure that I could display the proper signals and that I was interpreting the signals correctly.

I used one primary method to solve my problems on the days lacking progress and productivity: walk away. This was an extremely hard routine for me to adopt. Typically, I am a person who works through a project at hand until it is finished. I quickly found out that this approach does not work well for me personally when applied to experimentation. At the end of hours spent mulling over the current problem at hand, I would be no closer to a solution than when I started. I realized that when I get frustrated and impatient for results, my mind tends to fixate on trying to make my current approach work, even if it has continuously proven unsuccessful. As a result, my brain seems to be incapable of finding different solutions to try.

On the days I walked away from the experimental equipment, I decided to focus on the research end. I reread the apparatus manual, I looked over the NMR books I had checked out, and I looked for additional sources online. I decided to learn more about the theory itself instead of being consumed by one step in the experimentation process. I typically would not return to the lab until I had a new idea I wanted to try. While I cannot remember some of those specific ideas, I do know that most of them were not difficult or incredibly involved. The resolutions I came to were often small ideas that randomly came to mind. It appears I needed to give myself a break in

order to clear my thought process and find a solution that would work accordingly. I learned that I am capable of thinking outside of the box that is my usual thought process. I just need to give myself the proper time and patience to be able to get there.

I believe the knowledge gained during my thesis process will be beneficial in my future. It is a common requirement for physicists to complete a thesis project during graduate school. Though I am not going to grad school immediately, my experience with this experiment gave me an insight into what that process would be like. After talking to my advisor and working on this experiment myself, I know now that theses take far more time and effort than you anticipate, even if you assume at the beginning that it will be a long and involved process. I also realized that I can have better time management when it comes to experiments. If I hit a roadblock, I need to move on to another area of the project sooner. Not only will I remain productive by switching tasks, but I can allow my brain the time it needs to process what I have already done. That way I will return to the problem with a clear headspace. Thanks to this experience, I can approach my next thesis with a better game plan and the knowledge that with time things will begin to fall in to place.

I believe that my thesis better prepared me for future career paths as well. As an Applied Physics major, I will likely have a job that includes some level of experimentation. No matter the actual experiment, it is important to completely understand the physics behind whatever I am attempting. While I cannot predict the exact results, knowing the rules and laws of the physics involved will help me anticipate what behavior should be expected. Going into my NMR research, I did not have the slightest clue how the process worked. The beginning was difficult and met many roadblocks. As I got more familiar with the theory, however, things gradually became easier to understand.

Working on my thesis gave me my first real taste of experimental work, and I have a newfound appreciation for experimentation. The application of different physical processes and characteristics taught in the classroom provided an invaluable experience of hands-on learning. Patience and creativity are also crucial in order to overcome the problems that arise. My thesis taught me an invaluable lesson: you need to truly know and understand the laws and the absolute certainties of the physics involved. You need to take what you know to be true and apply it to the problem at hand. Prior to my thesis, most experiments I completed during my undergrad were focused on one specific law or theory. With my thesis, however, I had to apply various laws and theories at once, and the instructions did not tell me what they would be. Therefore, I was testing not only my knowledge on the new material, but any laws I had learned up to that point. Experimentation is by no means a quick or easy process and it can appear daunting at times. As a result, I believe it makes the triumphs and progress that much more rewarding.

Introduction

The purpose of this paper is to serve as an overview of my research on Nuclear Magnetic Resonance (NMR). NMR uses an intrinsic property of a proton, called spin, to reveal characteristics about the material the proton is in. The spins states can be manipulated by magnetic fields to change their energy and direction. Protons are located in the nucleus of an atom.

NMR in condensed matter was discovered separately but simultaneously by two scientists in 1946 [1]. Edward Purcell and Felix Bloch placed samples with magnetic nuclei in a uniform magnetic field. They then added an electromagnetic wave (EM) and observed how the nuclei responded. In 1950, Erwin Hahn was experimenting with radio frequency (RF) pulse bursts, and it is now the primary method used for NMR research [1]. This is the method used to conduct my experiments.

The simplest atom to experiment on would be hydrogen, as it only contains one proton. Hydrogen cannot be experimented on directly. On Earth, hydrogen is usually found as a gas but in order to be easily tested through NMR, it must be present as a solid or liquid. Achieving either solid or liquid form requires extremely low temperatures (-434.45 °F and -423.17 °F, respectively). The conditions must be maintained for hydrogen to remain in this state. To get around this issue, experiments can be done on materials that contain hydrogen. The material used in this paper was light mineral oil, and the experiments were conducted by using a Pulsed/CW NMR Spectrometer [1].

My first goal was to ensure it worked properly. Data was supplied with the apparatus to prove operation. Some of that work was replicated to make sure there was nothing wrong with it.

This equipment also has the potential to be used in the future. There are experiments that have not been completed, and there is the possibility for new experiments to be created. Therefore, my process has been detailed in the following pages. It is the groundwork for further experimentation with the apparatus.

The paper begins with the theory describing the NMR process. The next section gives an overview of the apparatus used for the experiments. There are also some general tips to ensure experimentation runs as smoothly as possible. From there is a discussion of the accomplished experiments. The paper concludes with remarks about future work with this technique.

The Physics

Particles can be described by a number of different properties. An example of such properties would be spin. Spin is an intrinsic angular momentum of a particle. The spin of protons will be studied in this paper. Protons have a spin $\frac{1}{2}\hbar$ and can exist in two energy states: $+\frac{1}{2}$ or $-\frac{1}{2}$. In the absence of a magnetic field, these two states will have the same energy.

NMR uses magnetic fields to alter a proton's spin. From this alteration, different measurements can be made. NMR begins with protons in a strong, constant magnetic field. The magnetic field causes the spins of the protons to align in its direction, and the protons precess around the field's axis. The magnetic field also causes the two energy states to no longer be equal; $+\frac{1}{2}$ becomes the lower energy state, and $-\frac{1}{2}$ becomes the higher energy state. A second, weaker, oscillating magnetic field can be added using an electromagnetic (EM) wave pulse that is at a radio frequency (RF). The RF pulse allows energy transfer, and some protons in the lower energy state can be boosted to the higher energy state. This causes the orientation of the protons to be altered. They now begin to precess around the new axis created by the second magnetic field. The effect is only temporary, however; eventually the second field will die out as time progresses from the time of the RF pulse. When that occurs, any protons that gained energy will return to their original states. As the spins return to their initial states, the gained energy will be emitted. The protons will realign with the constant magnetic field, but it does not occur instantaneously.

Proton spins are in randomly orientated directions. When an external magnetic field is added, the protons begin to precess along the direction of the magnetic field, similar to the

wobbling movement of a spinning top [2]. The rate at which the proton precesses is called the Larmor frequency (ω_0), given by

$$\omega_0 = \gamma \mathbf{B}_0, \quad (1)$$

where \mathbf{B}_0 is the magnetic field vector for the constant magnetic field mentioned earlier. The gyromagnetic ratio (labeled as γ in the equation) is a constant. For protons, γ is 2.675×10^8 rad/s-T or 42.6 MHz/T [1,2]. For experiments, \mathbf{B}_0 is created by a permanent magnet and is usually aligned along the z -axis. The Larmor frequency is the natural frequency of the system in question.

The magnetic field will cause the spins to align in its direction. The magnetic field also causes magnetization, meaning the sample will become magnetic or magnetized because all of the protons align. This leads to a magnetization vector, \mathbf{M}_0 . This initial magnetization of the protons is in the same direction as \mathbf{B}_0 . The field vectors are shown in Fig. 1. The vector \mathbf{M}_0

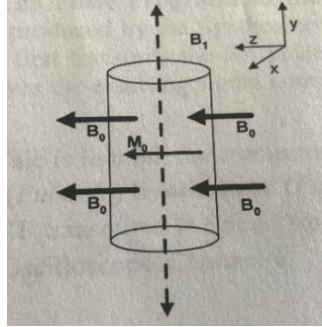


FIG. 1: Diagram of the field vectors. \mathbf{B}_0 is the constant magnetic field, \mathbf{M}_0 is the initial magnetization vector of the protons, and \mathbf{B}_1 is the magnetic field caused by the pulse [3].

cannot be measured by the apparatus. An oscilloscope will display signals appearing in the x - y plane, but the spins initially do not contain any transverse rotation (rotation that is perpendicular to \mathbf{B}_0 , and the x - y plane is also perpendicular to \mathbf{B}_0). This is because the spins are randomly oriented. When added together, the x - y components cancel each other out and do not create an

overall net component. It is similar to adding two sine waves that are out of phase, like the ones shown in Fig. 2. If you were to add the two waves together, the vertical components from each

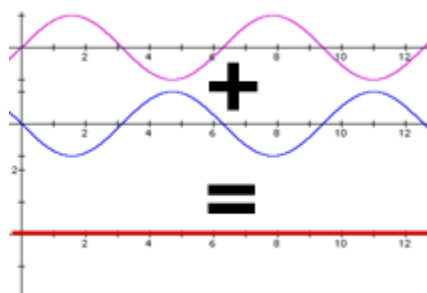


FIG. 2: Example of adding two sine waves that are out of phase [4].

wave would cancel each other out, causing the overall displacement to equal zero. The idea is similar for the spins of the protons. According to the apparatus, there is zero magnetization because no net spin direction can be seen in the x - y plane.

In order to observe the effects of NMR, an RF pulse is introduced perpendicular to the constant magnetic field \mathbf{B}_0 , and this pulse creates a weaker magnetic field \mathbf{B}_1 in the x - y plane, as shown in Fig. 1. This new field is used to alter the state of the protons. The RF pulse causes the precession of the proton spins to be in phase (all rotate together), rotates the proton spin direction into the x - y plane, and consequentially produces a transverse magnetization vector, \mathbf{M}_{xy} . The RF pulse needs to match the Larmor frequency of the protons in order to be able to affect their spins. The spins will only rotate if the RF pulse matches their natural frequency. The energy transfer that causes spins to change energy states will also be most efficient if the two frequencies match.

The coil will need to be tuned so that the RF pulses will have the same frequency of the protons. The more protons that are in phase, the greater the magnetization in the x - y plane. The protons are now precessing around \mathbf{B}_1 at a lower frequency than before. This is because the

frequency at which the protons precess is proportional to the field strength—shown in Eq. 1—and \mathbf{B}_I is weaker than \mathbf{B}_0 .

The spins are rotated by using RF pulses. We will be concerned with two types of pulses in order to achieve this: a 90° pulse and a 180° pulse. For a 90° pulse, the protons are flipped 90° , and the entire net magnetization vector is flipped into the x - y plane

$$\mathbf{M}_{xy} = \mathbf{M}_0. \quad (2)$$

On the experimental equipment, this 90° pulse corresponds to a pulse length around $2.50 \mu\text{s}$ [1]. The activity of the magnetization vector \mathbf{M}_{xy} following the pulse will be observed on the oscilloscope through a free induction decay (FID) signal. The FID signal indicates that the proton spins return to their original energy states after the 90° pulse is over. The FID begins immediately following the pulse [5]. Since the signal documents the protons leaving the x - y plane, the signal will be decaying.

It should be mentioned that the protons do not rotate instantaneously. For a 90° pulse, the rotation takes a time $\tau_{\pi/2}$ to occur. The time it takes to flip the spins the 90° is inversely related to the strength of the second field, \mathbf{B}_I , and it can be described by the equation

$$\tau_{\pi/2} = \frac{\pi}{\gamma \mathbf{B}_1}, \quad (3)$$

where π is a constant, γ is the proton's gyromagnetic ratio, and \mathbf{B}_I is the magnetic field vector in the x - y plane.

The concept is similar for the 180° RF pulse, only this time the net magnetization vector is being flipped 180° to $-\mathbf{M}_0$ (from the $+z$ -axis to the $-z$ -axis). This pulse is approximately twice the length of the 90° pulse (on the equipment it will correspond to a pulse length around $5.00 \mu\text{s}$ [1]). Since the pulse is twice the length, it also takes twice the amount of time to flip the protons as before. The time τ_π to achieve the 180° flip is represented in the equation

$$\tau_\pi = \frac{\pi}{\gamma B_1}, \quad (4)$$

which contains the same quantities as Eq. 3.

When the RF pulse is turned off, the proton spins will return to their original energy states and move out of phase again. The net magnetization vector will also realign with the direction of original magnetic field, \mathbf{B}_0 , along the z -axis (see Fig. 1). This is the spin rotation represented in the FID signal. Just like the spins cannot be flipped instantaneously, the spins cannot return to their initial state instantaneously either. The spins need to first dissipate any energy they absorbed during the RF pulse. The time it takes the spins to go back to their initial energy states is known as the spin-lattice relaxation time (T_1).

The spin-lattice relaxation time, T_1 , helps describe the state of \mathbf{M}_0 as it is recovering along the z -axis. After time t has elapsed following the RF pulse, a certain amount of the magnetization vector is again in the z direction. This is described by the vector $\mathbf{M}_z(t)$, which is dependent on time t . Their relationship is given by

$$\mathbf{M}_z(t) = \mathbf{M}_0(1 - e^{\frac{-t}{T_1}}), \quad (5)$$

where $\mathbf{M}_z(t)$ is the growing magnetization vector along the z -axis after the RF pulse, \mathbf{M}_0 is the original magnetization vector in the z direction before the RF pulse, t is the time elapsed, and T_1 is the constant spin-lattice relaxation time. As time increases, the magnetization \mathbf{M}_z will equal \mathbf{M}_0 . Equation (5) does not work for both pulse cases, however. It only holds for the condition that at time $t = 0$, $\mathbf{M}_z = 0$, which is true for a 90° pulse. For the other pulse we are concerned with, the 180° pulse, the same is not true. Here, at time $t = 0$, it is necessary that $\mathbf{M}_z = -\mathbf{M}_0$.

While the magnetization $\mathbf{M}_z(t)$ along the z -axis grows larger, the magnetization $\mathbf{M}_{xy}(t)$ in the x - y plane will grow smaller. The relationship is not exactly even, however; $\mathbf{M}_{xy}(t)$ will decay more quickly than $\mathbf{M}_z(t)$ grows. This is due to the spins of adjacent protons interacting with one

another. The frequency of one proton will affect the one next to it. Because of this, the time it takes $\mathbf{M}_{xy}(t)$ to decay is called the spin-spin relaxation time (T_2). After time t , $\mathbf{M}_{xy}(t)$ will be

$$\mathbf{M}_{xy}(t) = \mathbf{M}_0 e^{\frac{-t}{T_2}}, \quad (6)$$

where $\mathbf{M}_{xy}(t)$ is the decreasing magnetization vector in the x - y plane, \mathbf{M}_0 is the original magnetization vector along the z -axis, t is the time elapsed, and T_2 is the constant spin-spin relaxation time. This decrease in $\mathbf{M}_{xy}(t)$ will continue until the magnetization \mathbf{M}_{xy} equals zero.

While they appear similar, T_1 and T_2 are different quantities because they measure different processes. The first is looking at how long it takes the protons to return to their z -axis alignment. The latter describes how long it takes the magnetization vector in the x - y plane to disappear. Later, the experiments performed with the apparatus will focus on measuring both the T_1 and the T_2 of protons in different substances. Since these values are constant, the goal is to observe how these relaxation times compare for protons in different materials.

In order to measure T_1 and T_2 , it is better to use a two-pulse experiment. For this method, one pulse will be added to tip the spins, and then later a second pulse will be added to tip them again. For measuring T_1 , this two-pulse method will be accomplished in the experiments by having a 180° pulse followed by a 90° pulse. The 180° pulse will flip the protons to the negative z -axis. To find T_1 , the value for $\mathbf{M}_z(t)$ must be known, but the magnetization in the z direction cannot be measured directly. There is a quick fix to solve this problem: follow the first pulse with a 90° pulse. The 90° pulse flips the magnetization vector into the x - y plane. Therefore, immediately following the 90° pulse, the magnitude of $\mathbf{M}_{xy}(t)$ will be proportional to $\mathbf{M}_z(t)$ just before the 90° pulse.

In a two-pulse experiment, the time elapsed t will be equivalent to a quantity known as the delay time τ . The delay time is the time between the two pulses. As mentioned earlier, in the

case where the first pulse is 180° , Eq. 5 no longer holds. Here at $\tau = 0$, $\mathbf{M}_z = -\mathbf{M}_0$. Therefore, the magnetization vector in the z direction is described by a slightly different equation than Eq. 5

$$\mathbf{M}_z(t) = \mathbf{M}_0(1 - 2e^{\frac{-\tau}{T_1}}). \quad (7)$$

The difference is a factor of two in the exponential term. The variables remain the same.

The delay time τ between the occurrence of the two pulses can be set to different values. There is a specific delay time, however, that yields an FID signal amplitude of zero. At this time, the magnetization $\mathbf{M}_z(t)$ will also be zero. This time is referred to as τ_0 . Using Eq. 7, the value T_1 can be found at τ_0

$$T_1 = \frac{-\tau_0}{\ln(\frac{1}{2})}. \quad (8)$$

The spin-lattice relaxation time T_1 is one of the quantities that will be measured later in an experiment, and Eq. 8 is a useful way to obtain its value. The necessary delay time τ_0 will be a parameter set on the experimental equipment. In order to find the value of τ that yields $\mathbf{M}_z = 0$, τ needs to be varied until there is no FID signal.

The other way to find T_1 uses Eq. 7 directly, but the original magnetization vector \mathbf{M}_0 is an unknown value. Equation (6), which is used to find T_2 , also contains \mathbf{M}_0 . This magnetization vector cannot be directly measured, but an estimate of its value can be made from the exponential component of Eq. 7. When τ is very large, the contribution by T_1 is inconsequential, so Eq. 7 becomes $\mathbf{M}_z = \mathbf{M}_0$.

As an example, spin-lattice relaxation times for mineral oil are on the order of milliseconds [6]. After τ is properly chosen, such that $\tau \gg T_1$, the amplitude of the signal can be measured to find \mathbf{M}_0 . Then, Eq. 6 and 7 can be used to find the constants, T_1 and T_2 .

In order to find the spin-spin relaxation time T_2 , the first RF pulse will be 90° and the second will be 180° . When measuring T_2 , a spin echo will need to be used, as shown in Fig. 3.

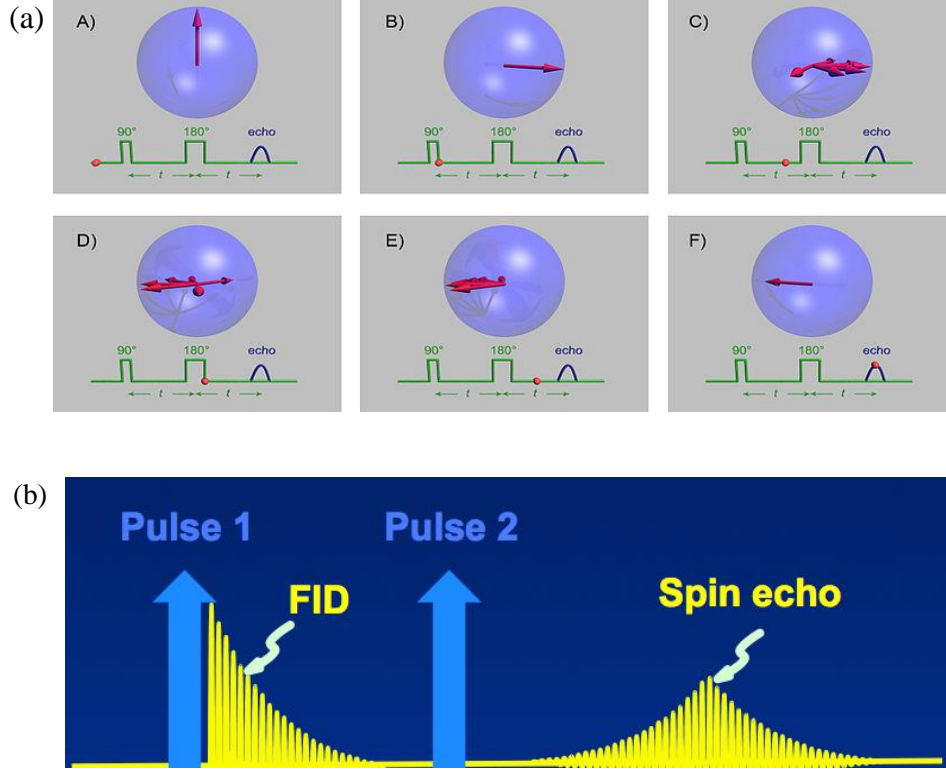


FIG. 3: The spin echo process. (a) Spin locations as time elapses and (b) graph of the FID signals. Pulse 1 is the 90° pulse, Pulse 2 is the 180° pulse, and the echo amplitude is used to find T_2 [7].

Figure 3(a) shows the spin direction as time elapses, and Fig. 3(b) displays the FID signal. The spin echo is an effect caused by having two successive pulses. After the 90° pulse, some spins may be in groups that precess slightly faster when compared to other groups, and there is a net component between them. In Fig. 3(a), the faster spins are toward the front of the sphere. This is because the local magnetic field may differ slightly on the microscopic level, causing somewhat different precession frequencies [7]. When the 180° pulse is applied, all of the spins flip directions. Now, the slower spin groups appear to be in the front of the sphere. The faster group of spins, which are now in the back of the sphere, will catch up with the slower spins [7]. When this occurs, an echo pulse will be produced, as shown in Fig. 3(b). The echo will appear at time

2τ after the 90° pulse (τ is still the delay time between the two pulses). The amplitude of the echo can be used to obtain $\mathbf{M}_{xy}(t)$, which can then be used with Eq. 6 to find T_2 .

The Instrument

The apparatus used for this study was designed by a company called TeachSpin [8]. The main components are shown in Fig. 4, and include a permanent magnet to generate \mathbf{B}_0 , a coil to

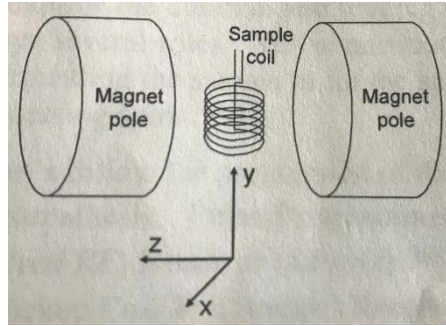


FIG. 4: Diagram of the experimental apparatus. The constant field \mathbf{B}_0 is supplied along the z direction by two magnet poles. The coil holds the sample and provides the RF pulses [3].

produce the RF pulses and detect signals, and an oscilloscope to display signals from a sample. The two cylinders in Fig. 4 (labeled magnet pole) are creating the stable magnetic field (\mathbf{B}_0). The field is horizontal between the two poles and along the z -axis. Figure 4 shows the configuration of the sample coil with respect to the magnetic poles. The sample coil sits in the center of the two poles. The sample material will be placed inside the coil. The coil transmits the RF pulses that create the second magnetic field, \mathbf{B}_1 . Figure 1 shows the field vectors. When the RF pulse is applied, the proton magnetization vector will tip away from the $+z$ -axis.

The coil detects the spin direction changes in the x - y plane and measurable data will be taken from the signals displayed on the oscilloscope. The oscilloscope displays voltage vs. time. The time axis will correspond with the delay time. The voltage axis will correspond with the amplitude of the vector $\mathbf{M}_{xy}(t)$ after the pulse. The oscilloscope can only display $\mathbf{M}_{xy}(t)$ (since it will be the only spin direction changes in the x - y plane), so the signal should always be

decreasing. A reminder that an M_{xy} vector occurs only after the RF pulse; as the effect of the pulse wears off and the protons return to their initial spin states, M_{xy} will disappear, as given by Eq. 6.

The spectrometer instructor's manual by TeachSpin details how to connect the electronics of the apparatus in a section called *Getting Started* [1]. In short, there is a mainframe that needs to be connected to the experiment. The mainframe has different modules that are responsible for different functions. The pulse programmer controls the pulses: which pulses are activated, how long they are, when they fire, whether or not they will fire more than once, etc. The pulse programmer also has switches to turn each pulse on/off. The synthesizer on the mainframe is the source of the RF signals used by the coil to tip the spins. After the spins have been tipped, the FID information is sent to the oscilloscope to be displayed. The signal on the oscilloscope is what is used to collect measurable data for the experiments.

Prior to testing samples, the RF solenoid holding the sample must be tuned as close to the Larmor frequency of the proton as possible. As stated before, the frequency of the RF burst must equal that of the natural frequency of the precessing protons in order to be able to tip their spins. This will also increase the amplitude of the signal. This is accomplished by using an RF pickup probe like the one seen in Fig. 5. There is a copper wire wound near the end of the probe. During



FIG. 5: RF pickup probe used to tune the magnet [1].

the pulse, the probe examines the field and feeds information directly to the oscilloscope. The amplitude of the signal will represent the frequency of the field. A frequency around that of the Larmor frequency will correspond with a signal amplitude of around 40 V. The probe is placed directly inside the sample coil. The copper wire must be in the center of the coil to ensure that it is entirely hit by the RF pulse. The position that yields the greatest peak for the signal on the oscilloscope will be the center of the coil.

The coil is what applies the RF pulses to the sample. In order to tune the system for the Larmor frequency, there are two tuning capacitors on the permanent magnet to the left of the opening to hold the sample, as shown in Fig. 6. The one on the left is used for coarse tuning

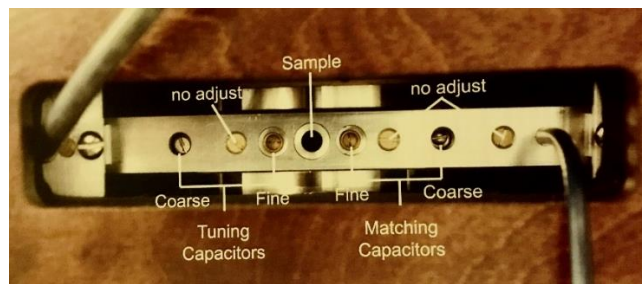


FIG. 6: Top view of the magnet. The tuning capacitors adjust the tension of the coil.

The hole labeled sample is where the pickup probe will be placed.

The matching capacitors will not be used [1].

(ranging from 25 – 150 pf), while the capacitor on the right allows for more fine tuning (ranging from 1 – 80 pf). The matching capacitors will not be touched. Adjusting the tuning capacitors changes the tension in the coil. The coil is wrapped around a tube that holds the sample. Adjusting the tension will change how tightly or loosely wound the coil is around the tube. This will then cause the frequency of the coil to change. The changing frequency will be accompanied by the amplitude of the signal changing on the oscilloscope.

When the coil is tuned close to the Larmor frequency of the protons, there will be a peak signal of around 40 V that is about 3 μs long. This is represented by the signals shown in Fig 7.

Figure 7(a) displays the signal (31.4 V peak-to-peak) obtained from my data. Figure 7(b) is the

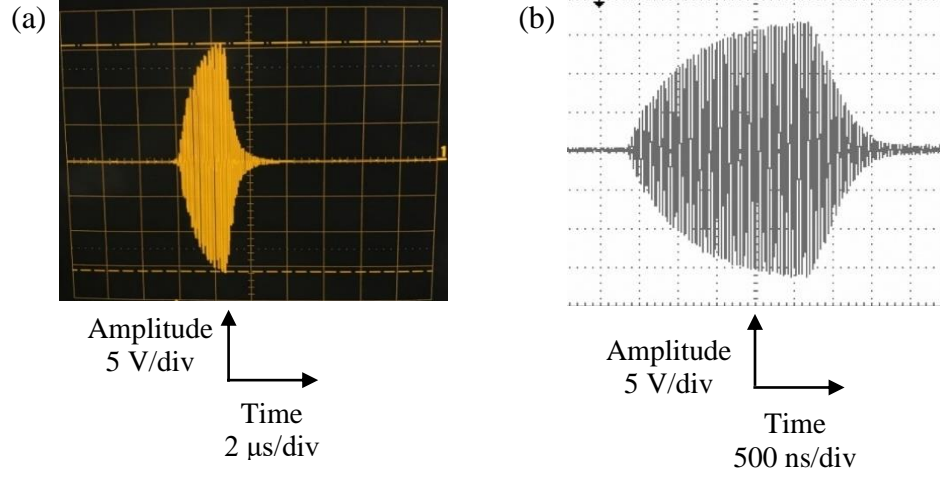


FIG. 7: (a) Signal for the frequency amplitude during the RF pulse and
(b) signal for the frequency amplitude provided by the manual [1].

example given in the manual. The pulses are comparable, but do not appear exactly the same due to their different scales. The coil was tuned using a 90° pulse. There are also various parameters, such as the pulse period, that can be adjusted to make the signal appear clearly and correctly.

Table I documents the values used to obtain Fig. 7(a).

TABLE I: Parameters and values used to tune the coil.

Parameter	Value
A_len	2.5 μs
Period (P)	100 ms
Sweep Times (horizontal axis of oscilloscope)	2 $\mu\text{s}/\text{div}$
Amplitude (vertical axis of oscilloscope)	5 V/div

After tuning the coil, the tuning capacitors remain fixed for all of the experiments.

On the pulse programmer, the pulse lengths dictate whether the RF pulse is 90° or 180° . The pulses are called A and B, and their lengths are designated by A_len and B_len, respectively. The lengths are measured in microseconds (μs). A 90° pulse corresponds to a pulse length of around $2.5 \mu\text{s}$. A 180° pulse (which is twice the duration as the 90°) corresponds to a pulse length of around $5.0 \mu\text{s}$.

Experiments

There are some measurement exercises designed to familiarize the user with the equipment. The first introductory experiment looks at the free induction decay (FID) of protons in mineral oil. A reminder that the FID is the signal in the x - y plane that appears after the 90° pulse. We should expect that the FID signal decays as time progresses. The writers of the manual accomplished this by using heavy mineral oil, but my experiments used light mineral oil. I do not expect to see great differences between the two.

The sweep times on the oscilloscope need to be adjusted for a longer time frame, between 0.5 and 1.0 ms/div. Before with the pickup probe, we were only looking at the signal during the pulse, and the pulse is only a few microseconds long. The FID of the protons starts the moment the RF pulse occurs and lasts until the magnetization M_{xy} disappears. The time for this process to complete is on the order of milliseconds. The longer sweep times allow for the whole FID signal to be displayed on the screen at once. The RF pickup probe will not be used in any of the experiments.

In order to flip the maximum number of protons, the sample must be placed in the center of the RF solenoid coil. Figure 8 shows the proper technique of preparing the sample. Only around 5 mm of sample should be placed in the tube, because using too much liquid will result in measurement errors. This means that calculated measurements may vary from the true value. The stopper-ring should be placed 39 mm above the center of the sample. This guarantees that the sample is placed directly in the center of the coil. This is to make sure that the maximum number of protons are exposed to the RF pulse. The larger the number of protons that experience the RF pulse, the greater the magnitude of the magnetization vector after they are flipped. This will

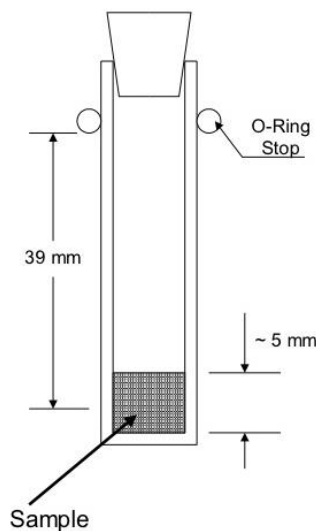


FIG. 8: Diagram with measurements of how to prepare the sample for experimentation [1].

produce a stronger signal on the oscilloscope, making it easier to calculate T_1 and T_2 . A sample position higher or lower than recommended will cause a smaller number of protons to be flipped by the RF pulse. This will make the signal amplitude smaller, and it will be harder to obtain correct values for T_1 and T_2 .

The sample can now be placed in the field created by the magnet. The vial is placed in the sample hole denoted in Fig. 6. Figure 9(a) displays the FID signal for light mineral oil. Figure 9(b) is the example provided in the manual for heavy mineral oil. Figure 9(a) has a smaller amplitude and a shorter decay time than Fig. 9(b). Based on the images, there appears to be differences in the FID of light mineral oil compared to the FID of heavy mineral oil. As for the decay time, I would assume that the T_1 for light mineral oil would be less than the T_1 for heavy mineral oil. The vertical displacement on Fig. 9(a) is negligible. What is important in Fig. 9 is that both FID signals decay exponentially. The vector \mathbf{M}_{xy} appears immediately after the pulse and decays as time elapses. Since my signal exponentially decays as expected, I took this to

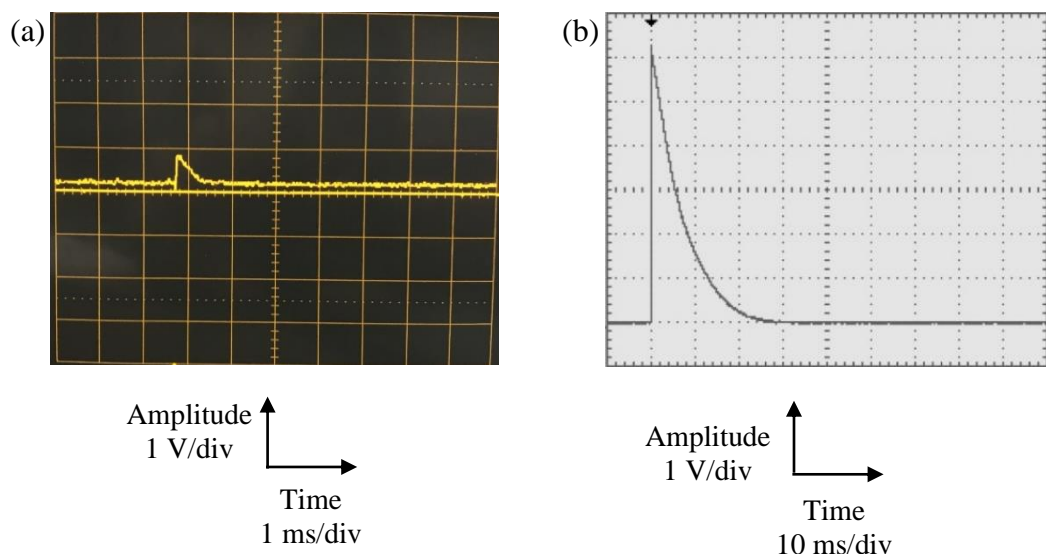


FIG. 9: (a) Signal for the FID of light mineral during a 90° pulse and
(b) signal for the FID of heavy mineral oil provided in the manual [1].

mean that the 90° pulse was indeed working.

There are a variety of parameters that can be adjusted on the mainframe modules. The manual suggests specific ones may be varied, and each will have a different effect on the received signal. Table II documents what measurement were observed while varying each

TABLE II: Results on the signal of adjusting various mainframe parameters.

Parameter Adjusted	Original	Observed Change
A_len (the pulse length)	$2.5 \mu\text{s}$	2.5 produces the largest peak. Either higher or lower, the signal amplitude shrinks.
Period	100 ms	At $P = 100 \text{ ms}$ there is one image. Smaller periods result in more peak signals appearing on the screen. No observed change for larger periods.
Frequency	21.0 MHz	21.2 MHz appears to be the peak. Larger or smaller and the signal amplitude decreases until it disappears.
Magnetic Field Gradients	0	Changing Z pinches the graph together, making it seem that the signal decays much more quickly.
Sample Placement in Solenoid	Center of coil	Amplitude of signal decreases whether the sample is moved higher up or pushed lower down.

parameter. The pulse (whether is it 90° or 180°) is dictated by the pulse length. For single pulse experiments, only pulse A will be used. The period sets how long it will take the pulse cycle to be completed. The Table II frequency is the frequency of the synthesizer that produces the RF signals. The magnetic field gradients help create optimum homogeneity in the permanent magnetic field (though TeachSpin says this is not required for many experiments [1]).

After obtaining a successful 90° pulse, the next task is to generate a 180° pulse. Since the 180° pulse is twice the duration of a 90° pulse, A_len needs to be changed to twice as long as before (it will now be around $5.00\ \mu\text{s}$). For a 180° pulse, the entire magnetization vector is flipped from $+z$ to $-z$. There should be no (or very small) FID signal after the pulse. If the entire vector is truly flipped, there is no component in the x - y plane to be monitored. If there is no M_{xy} , then there is no FID signal to be measured.

There are two adjustments that can be made to obtain a true 180° pulse: adjust the pulse length and alter the tuning capacitor. The primary one I focused on was the pulse length. The pulse length used falls between 5 and $6\ \mu\text{s}$. Figure 10 is the signal obtained while looking for a

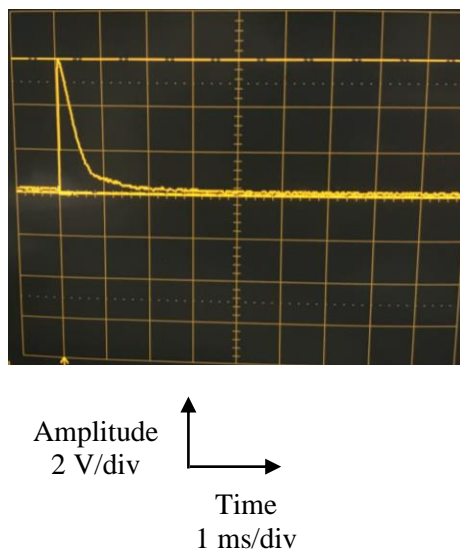


FIG. 10: FID signal for light mineral oil after a 180° pulse.

180° pulse, but it looks far more like a 90° pulse. After a true 180° pulse, there should be no FID signal. A better method would have been to examine both parameters, alternating between changing the pulse length and slightly adjusting the tuning capacitor until a null appeared following the 180° pulse. This will likely affect the results of data using 180° pulses.

Once single pulses have been mastered, it is time to move on to two-pulse experiments. This is the method that will be used later to measure T_1 and T_2 . Still using the light mineral oil, I wanted the first pulse to be 180° ($A_{len} \approx 5.00 \mu s$) and the second pulse to be 90° ($B_{len} \approx 2.50 \mu s$) to measure T_1 . After the B pulse is turned on, an important step needs to be taken. There is an option on the pulse programmer menu labeled N for Num_B. This setting will tell the apparatus how many times to fire the B pulse. It needs to be turned to at least 1 for the B pulse to fire at all (in comparison, the A pulse can only fire one time). If Num_B is greater than one, the oscilloscope will pick up signals for more B pulses and their corresponding echoes. For example, if $Num_B = 2$, there will be a signal showing a peak for a 180° pulse, a 90° pulse peak, an echo peak, another 90° pulse peak, and another echo peak. Pulse echoes were not seen during the single pulse experiments because they are caused by two successive pulses, like the ones used in two-pulse experiments.

Figure 11(a) is a signal obtained from two pulses. Table III is the corresponding set of parameters to achieve the signal. The first peak is the 180° pulse, the second is the 90° pulse, and the third is a spin echo, similar to what Hahn discovered. Note that the time between the echo and the second pulse is around the same as the time between pulses A and B, which again is known as delay time τ . The time differences should indeed appear the same. That was one of Hahn's discoveries when he first found the spin echoes. Figure 11(b) serves only to show an example of the spin echo. The pulses are actually in the reverse order than what I used. Figure

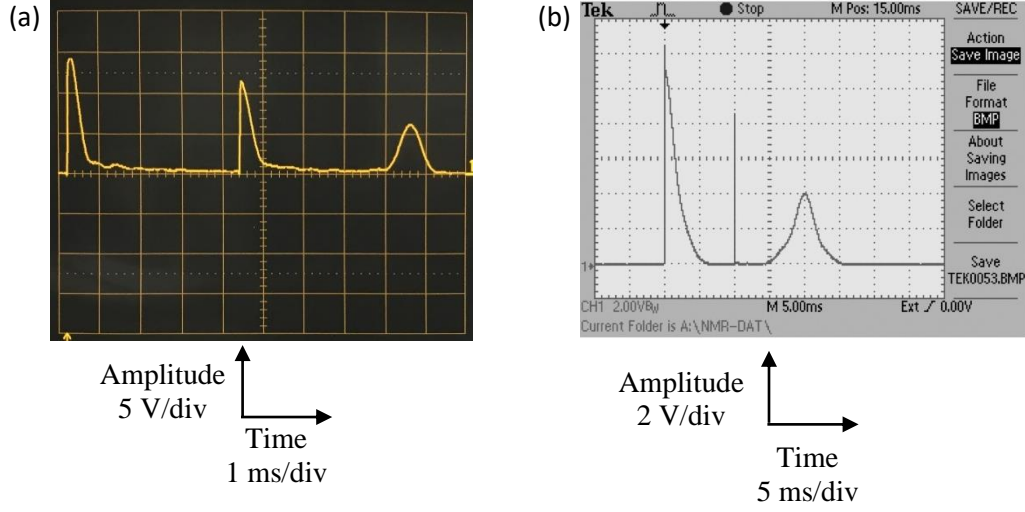


FIG. 11: (a) Signal for the 180° pulse followed by a 90° pulse and
(b) Sample signal of a two-pulse experiment and resulting echo taken from the manual [1].

TABLE III: Parameter values to obtain the signal in Fig. 11(a).

Parameter	Value
Frequency (F)	21.19500 MHz
A_len	5.42 μ s
B_len	2.52 μ s
Tau (τ)	0.0042 s
Num_B	1
Period (P)	480 ms

11(b) has a 90° pulse followed by a 180° pulse. The order and value of the pulses does not matter; when two pulses are successively fired, an echo will be produced. I would like to point out, however, that the spiked peak in Fig. 11(b), the middle “peak”, is how the true 180° should appear.

The next step is to measure T_1 for light mineral oil. The spin-lattice relaxation time T_1 is how long it takes for the magnetization vector to return to the $+z$ direction. The first way that this can be done is by finding the specific delay time τ_0 such that the FID signal is zero and using Eq. 8. The value for τ can be varied on the pulse programmer. It is important to note that the portion

of the signal that will change in Fig. 11(a) when adjusting τ is the middle peak—the one corresponding with the 90° pulse—so that is the peak that must go to zero. The signal following a 90° pulse represents the value for the $M_z(t)$. In order to use Eq. 8, the condition $M_z = 0$ must hold.

Figure 12 is the signal used to obtain M_z is 0, which should be a straight line at zero. I

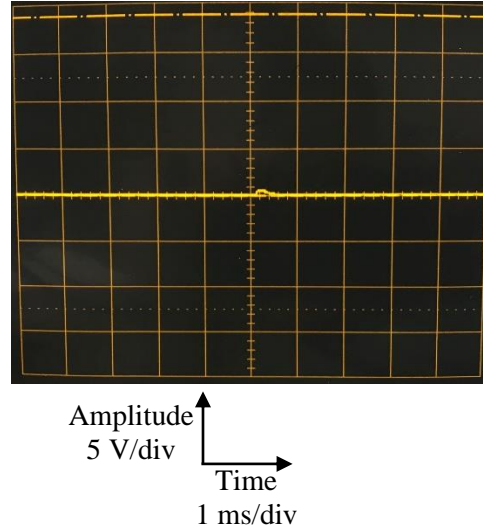


FIG. 12: Signal obtained when looking for $M_z = 0$.

was unable to get the FID signal to completely disappear, however, so the amplitude of the pulse is actually $M_z = 0.55$ V, corresponding with the small bump seen in Fig. 12. Here, $\tau_0 = 0.0233$ s, and the rest of the parameters remain the same from Table III. Using $\tau_0 = 0.0233$ in Eq. 8, I found that $T_I = 0.0336$ s, or 33.6 ms.

I attempted to find a value of T_I for mineral oil in order to compare my results. I found three different values: 20 ms, 60 ms, and 25.4 ms [6, 9,10]. None of the sources specified whether they used light or heavy mineral oil. Based upon the comparison data, the value I calculated for T_I appears consistent with at least two of the values found.

The second method is to extract T_I from a plot of the magnetization versus time. A graph of the various measured amplitudes with respect to their corresponding τ values is displayed in Fig. 13. All of the other parameters remained the same from Table III. Immediately two

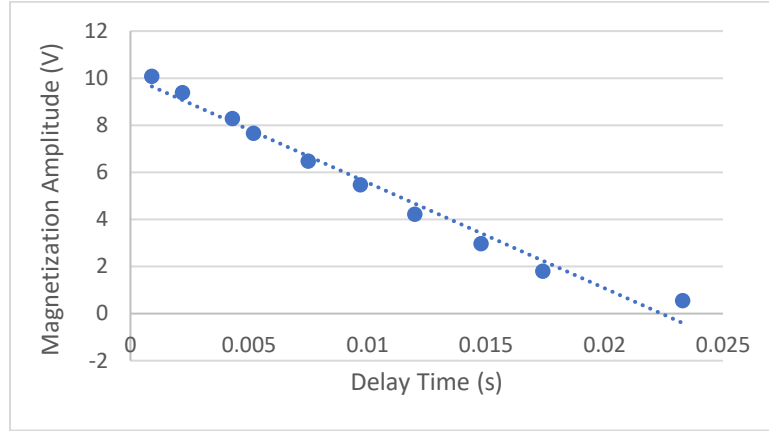


FIG. 13: Plot of the measured magnetization amplitudes as a function of delay times that is used to determine T_I . The dashed line is included to guide the eye

problems can be seen. First, τ is consistent with a linear function when it should be exponential. Second, the signal is decreasing when it should in fact be increasing. The time T_I is supposed to measure the how long it takes \mathbf{M}_z to recover along the positive z -axis. That means \mathbf{M}_z should be getting larger with time, not smaller.

A possible explanation of the discrepancy may be due to data collection. The initial pulse flipped the spins 180° degrees, and the oscilloscope displays magnetization signals in the x - y plane. At $\tau = 0$, $\mathbf{M}_z = -\mathbf{M}_0$, which means the protons are changing spin directions from the $-z$ axis to the $+z$ axis. As a result, the first \mathbf{M}_z values will be negative and pointing along the $-z$ axis. The middle point is the τ_0 value that corresponds with $\mathbf{M}_{xy} = 0$, which was found earlier. Any $\tau < 0.0233$ s will yield signal amplitudes for the $-\mathbf{M}_z$ values, and any $\tau > 0.0233$ s will yield signal amplitudes for the $+\mathbf{M}_z$ values. Data were collected that occurred before the zero point. Figure 13

shows data for the magnetization vector along the negative z -axis, which makes some sense; that signal should be decaying as the protons realign with the positive z -axis. Figure 14 shows an

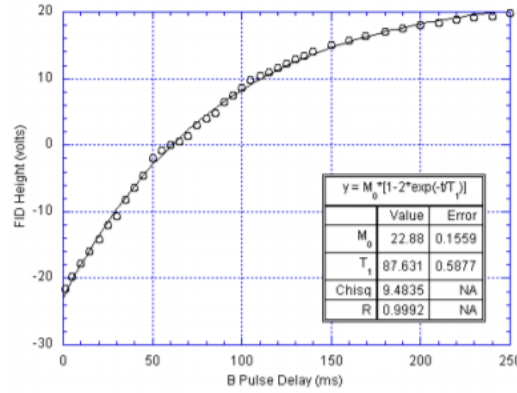


FIG. 14: Example of the expected graph to use to measure T_1 [9].

example of the expected results from the data [9].

In order to obtain a graph resembling Fig. 14, data occurring *after* the zero point of the signal would need to be collected and used. After plotting those values, a function that best represents the data would need to be fit to the graph. From the fit equation and Eq. 7, a value of T_1 can be extracted. That value of T_1 would then be compared with the value of T_1 calculated from the first method.

The next step would be to measure T_2 using the spin echo mentioned earlier. This method uses a 90° RF pulse followed by a 180° pulse. The signal should resemble Fig. 10(b). The echo amplitude can be plotted as a function of two times the delay time τ in order to find T_2 . No data was recorded that could lead to a value for T_2 .

After these T_1 and T_2 measurements are made, the same methods to measure the relaxation times can be repeated with a new vial of light mineral oil. This can be done a few times in order to obtain an average value for both relaxation times. There are some other

introductory experiments with multiple echoes that can be done and other samples besides mineral oil. There are also experimental options to focus on fluorine instead of hydrogen.

Conclusion

This paper details my work with NMR. I did research to familiarize myself with the physics that explains the method. All of the work I completed was done on light mineral oil provided by TeachSpin. While working with the apparatus, I first needed to tune the sample coil in order to be able to flip the spins of the protons. The next task was to get familiar with the two different RF pulses: 90° and 180° . I attempted to reproduce the expected FID signals after each pulse. After that, I used the two-pulse method to try and find the spin-lattice relaxation time (T_1) and the spin-spin relaxation time (T_2). The value I calculated for T_1 was 33.6 ms.

I have a few words of advice pertaining to this experimental process. First, make sure the physics is completely understood. It makes interpreting the data far easier and potential problems can be spotted more quickly. I would also suggest trying to write about the data after each step to make sure it is in accordance with the physics. I believe I have learned more in the writing of paper than while I was taking measurements. A great deal of time and patience is also required. The solutions to problems that surface are not always immediate or obvious. Sometimes it requires an idea not tried before or a fresh, clear headspace. Progress requires a great deal of dedication.

In the future, more work can be added on to the groundwork laid down. I am convinced that the equipment works properly. The data can be analyzed for the T_1 and T_2 of light mineral oil, and the methods to calculate these times can be applied to other materials. There are other introductory experiments for spin echoes as well. There is also a whole section on fluorine not covered here since I was focused on hydrogen. Overall, this experimental equipment still holds

numerous possibilities. I believe that this apparatus can serve as a useful hands-on learning experience for someone else that wishes to get familiar with NMR.

NMR is a unique and non-invasive way to learn about the behavior of particles in substances. The Magnetic Resonance Imaging (MRI) devices used by doctors is the most well-known application to the general public. Some of the medical applications include: MRI mammography, fingerprinting, and radiation therapy [11]. NMR is not limited to medicine, however. Chemists can use the technique to determine the structure of compounds. NMR is even being used by oil refineries and petrochemical plants to control and optimize unit operations. There appears to be a number of useful applications of this technique in a variety of fields.

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